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Fe@Pd/C: An efficient magnetically separable catalyst for direct reductive amination of carbonyl compounds using environment friendly molecular hydrogen in aqueous reaction medium

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ABSTRACT

Direct reductive amination of carbonyl compounds with variety of amines has been reported by using magnetically separable Fe@Pd/C as an efficient catalyst in aqueous reaction medium. The developed methodology offers synthesis of various secondary and tertiary amines using different aldehydes and ketones with amines giving excellent yield. Moreover, the magnetically separable Fe@Pd/C catalyst was easily separated from reaction mixture and can be recycled for further reaction.

1. Introduction

Amines are highly versatile building blocks for various organic substrates and have wide applications in the pharmaceutical, agrochemical, chemical industries, materials science, and biotechnology [1–3]. Direct reductive amination of aldehydes and ketones with primary or secondary amines is one of the powerful and widely used C—N bond formation reactions for the synthesis of substituted amines in synthetic organic chemistry. In the last two decades, many research groups reported versatile strategies for the synthesis of substituted amines by the direct reductive amination method. To attain this conversion, use of various boron based hydride reagents has been developed, including $NaBH_4$ [4], zinc borohydride [5], sodium cyanoborane [6], pyridine-BH_3 [7], $InCl_3/Et_3SiH$ [8]. Nevertheless, above mentioned methods requires stoichiometric metal hydride source, cyanoborohydride reagents are extremely poisonous, which leads contamination of products with toxic by-products, besides some hydride source pyridine-BH_3 is highly unstable to heat and therefore need to take extreme care while handling.

Recent development in direct reductive amination includes the use of gold catalyst in the presence of silane [9], poly(methylhydrosiloxane) PMHS [10] and palladium based catalysts [11] were also reported. Direct reductive amination under transfer hydrogenation method has been investigated by Hu et al. and Xiao group [12]. However, the above mentioned methods have some drawbacks such as hazardous by-products, requires an acidic condition, harsh reaction condition, use of organic solvents and homogenous catalytic system which lead to problem of catalyst–product separation from the reaction mixture. Considering these drawbacks efforts were taken to develop improved heterogeneous recyclable catalytic system for direct reductive amination using environmental-friendly molecular hydrogen as a clean hydrogen source under mild reaction condition.

Nowadays, the use of water as a reaction medium has attracted considerable attention since water is an inexpensive, safe, readily available and non toxic solvent hence provides remarkable advantages over organic solvent [13]. Recently we have reported aqueous biphasic catalytic system for direct reductive amination of carbonyl compounds using polymer supported palladium complex [14]. Other reports from group of Ajjou [15a], Ogo et al. [15b] and Xiao et al. [15c] were also explored water as a reaction medium. Therefore, the hydrogenation of organic molecules in a water phase offers a simple solution for recycling the catalyst, and improves the products/catalyst separation.

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Recently, bimetallic transition metal core–shell nanoparticles (NPs) with magnetic properties have attracted great attention in catalysis, organometallic chemistry, biotechnology and magnetic resonance imaging. These magnetic nanoparticles were easily separated by using an external magnetic field, therefore offers the advantage of recyclability [16]. Palladium is a versatile catalyst and its nanoparticles have been widely used for various organic transformations as NPs have a high surface area and excellent catalytic activity. Generally the catalytic reaction take place on the surface of palladium nanoparticles and remaining part of palladium is inactive especially the core [17]. Therefore, it is challenging to use entire palladium atom to decrease Pd loading without affecting its catalytic activity. Herein, the concept of core shell has been introduced to overcome these difficulties and gaining the attention toward bi-metallic catalytic system [18]. In this core shell, palladium is substituted by other transition metals like Ni, Fe and Co which significantly improves catalytic activity due to the electronic and structural rearrangement of the two metals [19]. Recently, Li et al. have also explored magnetically separable Fe@Pd/C catalyst for Suzuki reaction in aqueous medium [20], this catalytic system offers several advantages like reuse of precious palladium metal by using magnet, avoids possibility of metal contamination in products and shows high catalytic activity in aqueous reaction medium. Hence, these results encourage us to explore Fe@Pd/C catalyst for direct reductive amination reaction. On continuing the exploration of new catalytic systems for direct reductive amination [21] herein, we report core–shell Fe@Pd/C as a versatile catalyst for direct reductive amination of carbonyl compounds with primary and secondary amines using environmental-friendly molecular hydrogen in aqueous reaction media.

2. Experimental

All the chemicals and metal precursor were procured from reputed firm and was used without further purification. The catalyst Fe@Pd/C was prepared according to the reported procedure in the literature and was characterized with various analytical techniques [20].

2.1. Catalyst preparation

In a round bottom flask containing active carbon (200 mg) was added to nitric acid (2 M, 100 mL) and then heated at 80 °C for 3 h in order to remove impurities. The Fe@Pd core–shell structured nanoparticles were prepared with amorphous Fe with molar ratio of Pd:Fe = 1:20. In a round bottom flask, 100 mg dried active carbon and 289.6 mg of $FeCl_3$ were dispersed in 30 mL water. The resulting suspension was kept in sonicator bath for 20 min. Then aqueous solution of $NaBH_4$ (676.2 mg in 90 mL water) was added dropwise into reaction mixture to reduce Fe^{3+} to Fe^0. The reaction mixture was then shaken vigourously till all hydrogen gas releases completely. The Fe/C NPs were then collected using magnet and washed with water and ethanol to remove excess of $NaBH_4$. In next step Fe/C was suspended in water, to this suspension aqueous solution of $PdCl_2$ (0.09 mmol) was added dropwise and stirred for 1 h. The atoms in outer-layer of the Fe core were sacrificed to reduce Pd^{2+} to Pd^0. Finally, the catalyst was dried in a vacuum at 50 °C for overnight.

2.2. Characterization method

The X-ray diffractometer of catalyst was obtained on a Shimadzu Lab XRD-6100 with the scan speed of 2°/min over a range from 20° to 80° using the copper target with λ = 1.54 Å. Field emission gun-scanning electron microscopy (FEG-SEM) images were obtained using a TESCAN MIRA 3 model to study the morphology of prepared catalyst.

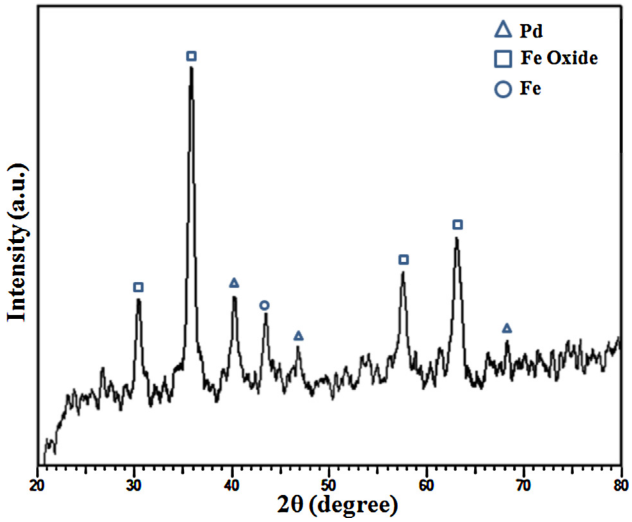

Fig. 1. XRD patterns of Fe@Pd/C.

2.3. Typical procedure for direct reductive amination of aldehydes with amines

To a 100 mL autoclave were added aldehyde (2.5 mmol) and amine (2.5 mmol) results the formation of imine, then catalyst (1 mol%), and water (15 mL) were added and reactor was closed. The reactor was then purged 3 times with nitrogen and finally reaction mixture was pressurized to 30 bar of hydrogen pressure. The reactor was heated to 80 °C and stirred for 8 h at 500 rpm. After completion, the reactor was cooled to room temperature and the remaining hydrogen gas was carefully removed. The catalyst was separated from reaction mixture by using magnet. The product from aqueous phase was extracted with ethyl acetate. The ethyl acetate layer was evaporated in vacuum by rotary vapour to obtain the product. All the products are well known in literature and were confirmed by GC (Perkin Elmer, Clarus 400) (BP-10 GC column, 30 m × 0.32 mm ID, film thickness 0.25 mm) and GCMS (Shimadzu GC-MS QP 2010) (Scheme 1).

3. Results and discussion

3.1. Catalyst characterization

The XRD pattern of Fe@Pd/C can be indexed with respective to 2θ of iron oxide, iron and palladium as shown in (Fig. 1). The Peaks in X-ray diffraction pattern of iron and iron oxide indicate the presence of magnetic properties of the catalyst. The XRD pattern of palladium clearly indicates the diffraction peaks occurs at 2θ values of 40.1°, 46.6°, and 68.0° can be assingned to the (1 1 1), (2 0 0) and (2 2 0) crystal planes, respectively.

The scannig electron microscope (FEG-SEM) image of of Fe/C NPs (Fig. 2a) showed that iron core supported on carbon which indicates the presence of small pores of Fe/C on the surface. In high resolution FEG-SEM image also shows that activated carbon is uniform in pores (Fig. 2b). Fig. 2c and d shows small particles of metallic palladium sitiuated on iron core which reveals outer layer of iron core–shell atoms was sacrificed with palladium. This was also confirmed by EDS mapping of Fe@Pd/C, the EDS mapping shows the presence of Fe, Pd and carbon.

In energy dispesive X-ray elemental mapping (Fig. 3) for Fe@Pd/C shows that presence of Fe (green), Pd (red) and carbon

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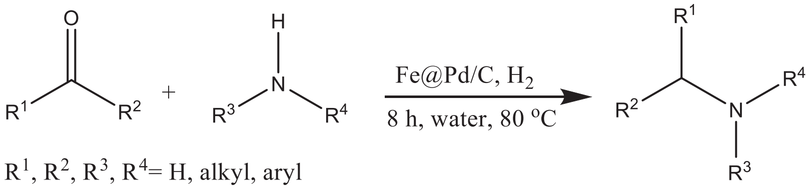

Scheme 1. Direct reductive amination of carbonyl compounds with amines in aqueous medium.

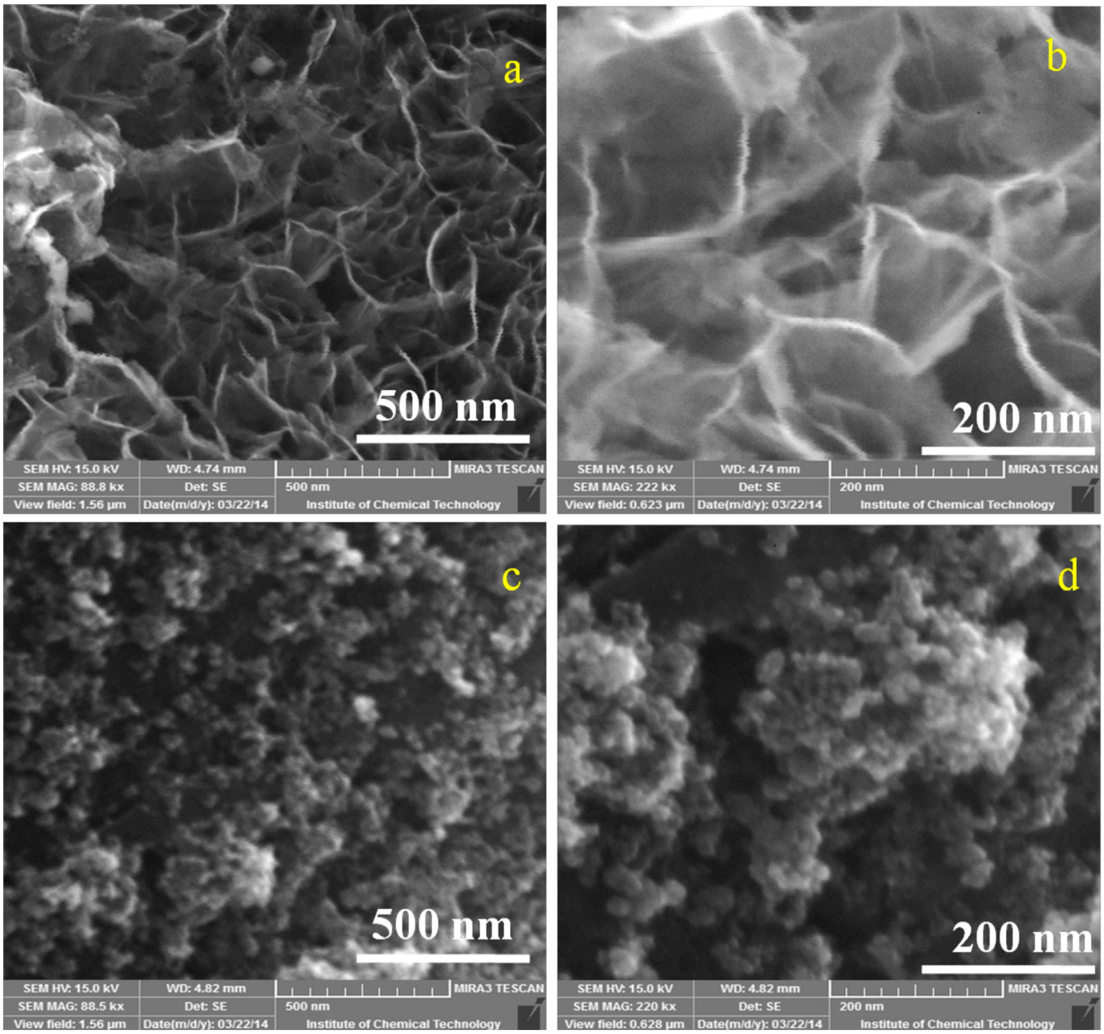

Fig. 2. FEG-SEM images of Fe/C (a and b) and Fe@Pd/C (c and d).

(blue) species coexist in the material. In EDS mapping (Fig. 3) it was observed that the concentration of Pd (red) is lower than the Fe (green). The heterogeneous Pd^{2+} reduce on iron core shell at time of development of substitution of palladium. Thus, the obatined result reveals the formation of core-shell structure of Fe@Pd/C.

3.2. Study of optimization parameters for direct reductive amination in aqueous media

We checked the activity of Fe@Pd/C as a choice of catalyst for direct reductive amination of benzaldehyde with aniline in aqueous media as a model reaction. Various reaction parameters such as catalyst screening, catalyst loading, effect of hydrogen pressure, reaction temperature and time were investigated and obtained results are summerized in (Table 1). Among the screened calalysts, Fe@Pd/C furnish excellent yield of the desired products as compared to commercially available Pd/C, Ru/C catalysts. Whereas, using Fe/C NPs as a catalyst, trace of product formation was observed in aqueous medium (entries 1–4). Then, we checked the effect of catalyst loading ranging from 0.25 mol% to 1 mol%. It was observed that, there is gradual increase in catalyst concentration from 0.25 mol% to 1 mol%, the increase in yield of desired product was observed (entries 5–7).

Next, we studied the effect of hydrogen pressure; it was observed that increasing hydrogen pressure from 10 to 30 bar, increases the yield of desired product (entries 8–10). Further we have also studied the effect of temperature and time. The reactions were carried out at different temperature ranging from 40 °C to 80 °C, it was observed that 80 °C is the optimum temperature to get maximum yield (entries 11–13). Time study reveals that 8 h are sufficient to give excellent yield of desired product (entries 14–16). Therefore, the final optimized reaction parameters

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Table 1
Effect of reaction parameters on direct reductive amination in aqueous medium.[a]

Entry	Catalyst	Catalyst loading (mol%)	H_2(bar)	Temperature (°C)	Time (h)	Yield (%)[b]
Catalyst screening						
1	Pd/C	1	30	80	8	Trace
2	Ru/C	1	30	80	8	22
3	Fe/C NPs	1	30	80	8	Trace
4	Fe@Pd/C	1	30	80	8	96
Catalyst loading						
5	Fe@Pd/C	0.25	30	80	8	34
6	Fe@Pd/C	0.5	30	80	8	62
7	Fe@Pd/C	1	30	80	8	96
Effect of hydrogen pressure (bar)						
8	Fe@Pd/C	1	10	80	8	32
9	Fe@Pd/C	1	20	80	8	59
10	Fe@Pd/C	1	30	80	8	96
Effect of temperature						
11	Fe@Pd/C	1	30	40	8	18
12	Fe@Pd/C	1	30	60	8	54
13	Fe@Pd/C	1	30	80	8	96
Effect of time						
14	Fe@Pd/C	1	30	80	4	36
15	Fe@Pd/C	1	30	80	6	78
16	Fe@Pd/C	1	30	80	8	96

[a] Reaction conditions: benzaldehyde (2.5 mmol), aniline (2.5 mmol), water (15 mL), catalyst, hydrogen gas.
[b] Yields based on GC analysis.

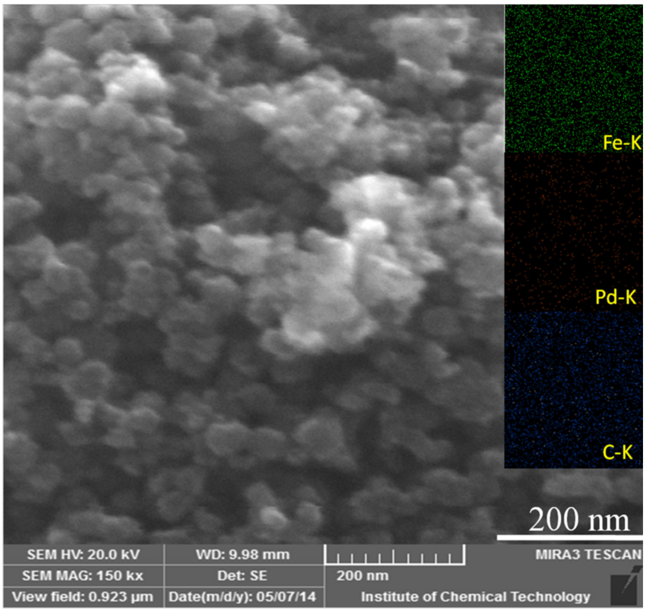

Fig. 3. Energy dispesive X-ray elemental mapping of Fe@Pd/C. (For interpretation of the references to color in the text of this figure citation, the reader is referred to the web version of this article.)

were benzaldehyde (2.5 mmol), aniline (2.5 mmol), water (15 mL), Fe@Pd/C catalyst (1 mol%), H_2 pressure (30 bar), temperaure (80 °C) and time (8 h).

With these optimized reaction conditions; we explored the developed protocol for the synthesis of wide variety of substituted amines by direct reductive amination in aqueous media (Table 2). The reaction of benzaldehyde with aniline gave corresponding secondary amine in excellent yield (entry 1). It was observed that both electron donating or withdrawing groups on aldehyde were well tolerated under optimized condition furnishing good to excellent yield of secondary amines, (entries 2–5). We found that various substituted aromatic amines react smoothly with benzaldehyde giving desired product in good yield (entries 6–9). Naphthalen-2-amine also reacted smoothly with benzaldehyde giving good yield of desire product (entry 10). Next, we treated various benzyl amine derivatives and pharmaceutically important 1-phenylethanamine with benzaldehyde furnishing excellent yield of desired product (entries 11–13).

Further we tested our protocol for cyclic and aliphatic amines such as cyclohexyl amine, cyclopropyl amine and butyl amine reacts with benzaldehyde giving desired secondary amines in excellent yields (entries 14–16). The secondary amines such as morpholine and n-methyl benzyl amines were screened with benzaldehyde resulting in the formation of tertiary amines in good yields (entries 17, 18). Noteworthy to mention that cyclohexanone was also reacted with primary and secondary amines such as aniline and morpholine giving excellent yields of the corresponding product (entry 19, 20). Moreover, we have also screened heterocyclic amine such as 2-amino pyridine providing good yield of corresponding secondary amine (entry 21). Whereas, employing cinnamaldehyde with aniline furnished corresponding secondary amine with complete reduction of olefinic bond (entry 22). Acetaldehyde also provide appreciable yield with aniline giving desired product (entry 23).

Thus, the present methodology was found to be broadly applicable for direct reductive amination of various structurally and electronically diverse aldehydes and ketone with primary, secondary and heterocyclic amines providing good to excellent yield of corresponding secondary and tertiary amines.

3.3. *Recyclability study of Fe@Pd/C catalyst for direct reductive amination in water*

To make developed protocol more economical, recyclability of the Fe@Pd/C catalyst was studied for direct reductive aminnation in water. After complition of reaction, the reaction mixture was cooled to room temperature, then Fe@Pd/C catalyst was seperated by using magnet. The catalyst was then washed with water followed by ethanol to remove traces of organic compounds, dried in vaccum and used for further reaction (Fig. 4).

The catalyst could be reused up to four consecutive cycle without affecting its catalyitc acttivity for direct reductive amination (Fig. 5).

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Table 2
Direct reductive amination of carbonyl compound with primary and secondary amines using Fe@Pd/C as catalyst in aqueous medium.[a]

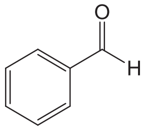
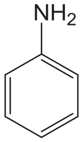
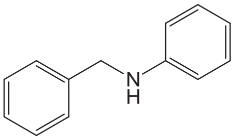
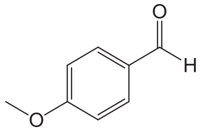
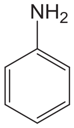
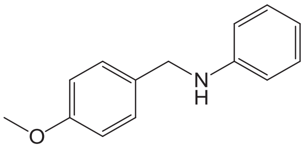
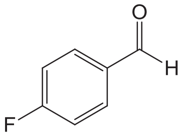
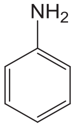
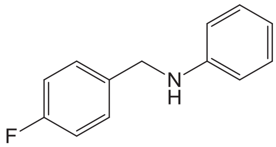
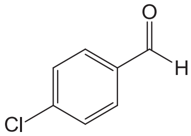
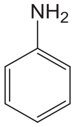
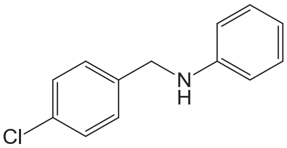
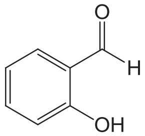
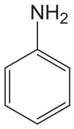
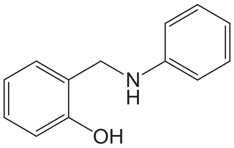
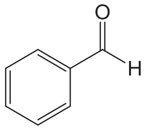
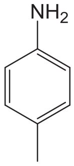
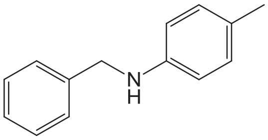
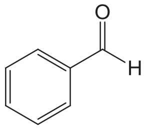
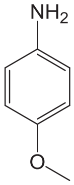
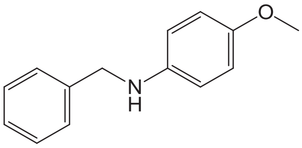
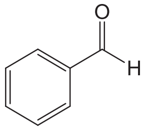
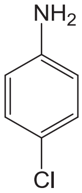
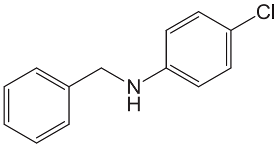
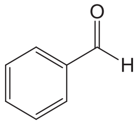
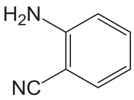
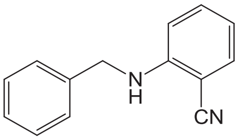
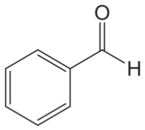
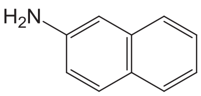
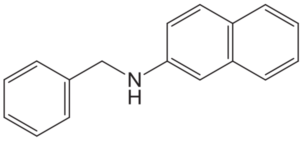
Entry	Aldehyde	Amine	Product	Yield (%)[b]
1				96
2				92
3				84
4				85
5				78
6				87
7				91
8				81
9				72
10				79

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Table 2 (*Continued*)

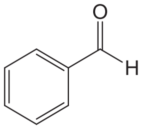
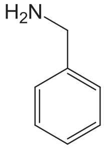
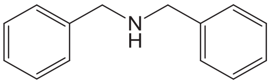
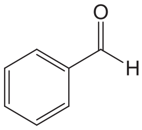
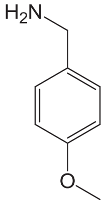
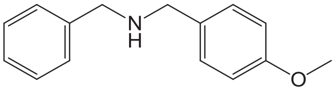
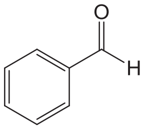
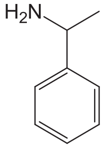
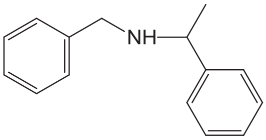
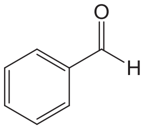
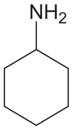
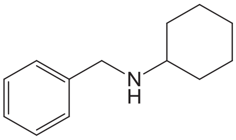
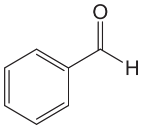
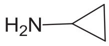
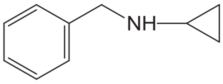
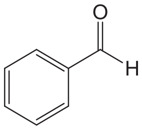
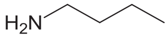
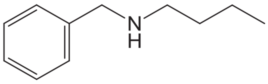
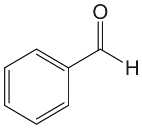
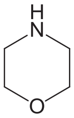
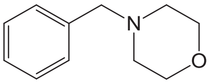
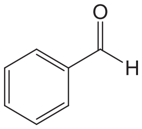
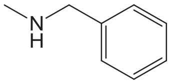
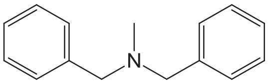
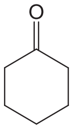
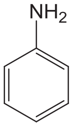
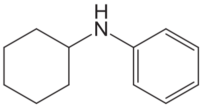
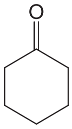
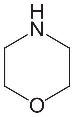
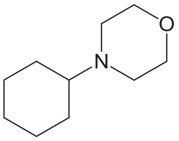
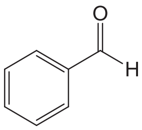
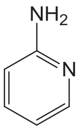
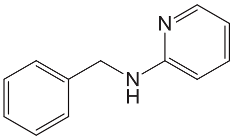
Entry	Aldehyde	Amine	Product	Yield (%)[b]
11				95
12				89
13				86
14				92
15				78
16				89
17				90
18				81
19				94
20				92
21				80

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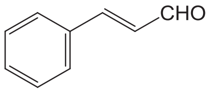
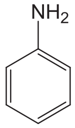
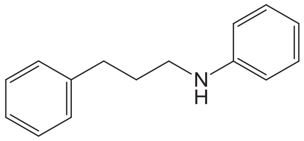
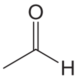
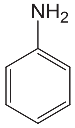
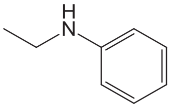
Table 2 (*Continued*)

Entry	Aldehyde	Amine	Product	Yield (%)[b]
22				91
23				82

[a] Reaction conditions: aldehyde (2.5 mmol), amine (2.5 mmol), Fe@Pd/C (1 mol%), Water (15 mL), H_2 press. (30 bar), temp. (80 °C), time (8 h).
[b] Yield based on GC analysis.

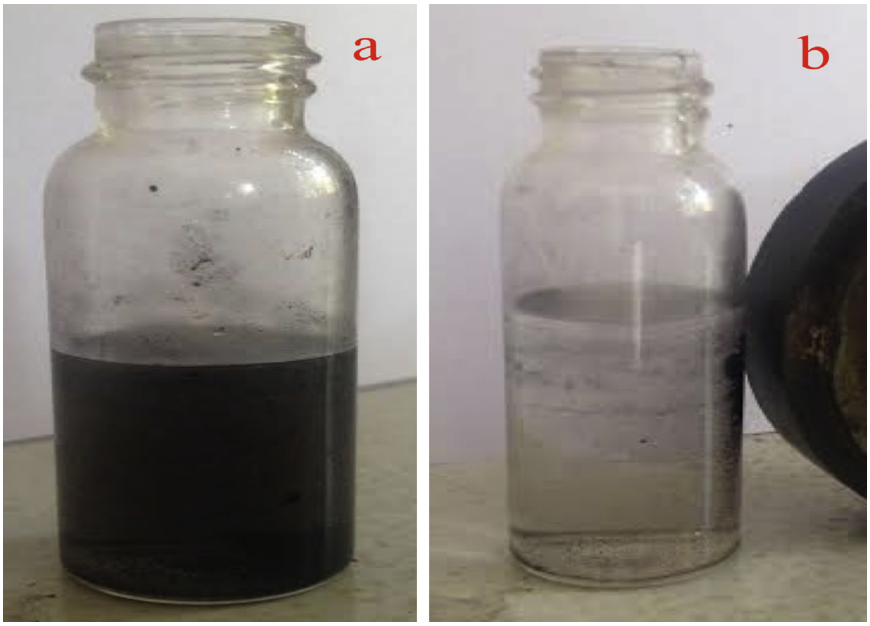


Fig. 4. (a) Catalyst suspension before applying magnet, (b) after applying magnet.

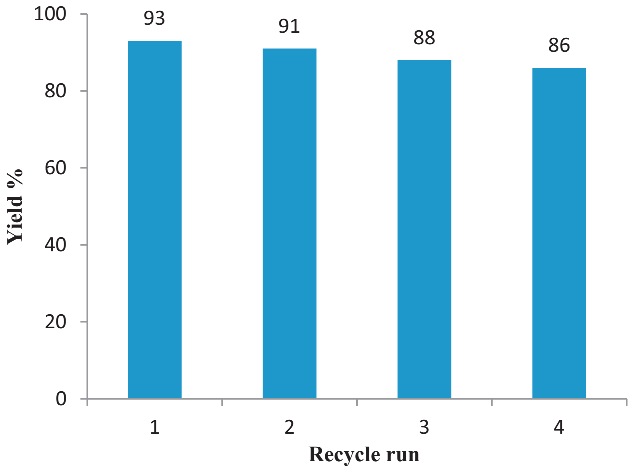


Fig. 5. Catalyst recyclability study for direct reductive amination in aqueous media.[a]
[a]Reaction condition: benzaldehyde (2.5 mmol), aniline (2.5 mmol), water (15 mL), Fe@Pd/C (1 mol%), H_2 pressure (30 bar), temperaure (80 °C), time (8 h).

4. Conclusion

In conclusion, we have developed simple, efficient, greener protocol for the synthesis of higher substituted amines by direct reductive amination of carbonyl compounds with various amines in aqueous media. The prepared Fe@Pd/C catalyst is highly stable and shows excellent activity in water for direct reductive amination reaction. The catalyst (Fe@Pd/C) was easily separated from reaction mixture by magnet and could be reused up to four successive cycles without losing its catalytic activity. The developed protocol is more advantageous due to use of water as environmentally benign solvent and effective catalyst recyclability.

Acknowledgments

The authors (N.M. Patil) are grateful to UGC-SAP (University Grant Commission, India) for research fellowship and also acknowledge for Nano Mission Project (No.SR/NM/NS-1097/2011) supported by Department of Science and Technology, Govt. of India for providing financial support.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2014.07.057.

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